Ab initio interatomic potentials of cubic boron nitride

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Abstract

Chen's lattice inversion method is extended to calculate the interatomic potentials of the zinc-blende-type binary compounds with a virtual lattice technique, which proposes a scheme to obtain non-empirical interatomic potentials from first principle calculations. In this paper, the interatomic pair potentials Φ_{N-N}, Φ_{B-B} and Φ_{B-N} are obtained from the ab initio cohesive energy curves relevant to the three distinct BN structures. The modified Stillinger–Weber (MSW) three-body potentials are determined by the dependence of the total energy on the lattice distortion. Based on the calculated interatomic potentials, the structural properties and lattice dynamics of cubic boron nitride (c-BN) have been evaluated.
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1. Introduction

The interatomic potentials are widely used in the investigation of the structures, defects, and dynamical properties of various materials. A number of empirical interatomic pair-potential forms such as the rigid-sphere model, Buckingham potential, Lennard–Jones potential, Morse potential and Born–Mayer potential [1] etc., have been developed. In the early 1980s, Carlsson, Gelatt, and Ehrenreich (CGE) developed a non-experiential pair potential with an iterative form [2], and this is the first attempt to obtain the interatomic potentials from the cohesive energy curves analytically. The CGE approach has been applied to many calculation works with success by only a couple of authors [3,4]. In 1990, a number-theoretic Möbius inversion method [5,6] was applied creatively to a few physical inversion problems, which results in the solution to a series of problems such as the capacity inverse problem [7], the lattice inverse problem [8] and the inverse problems in astrophysics [9] etc. It is worthy of mention that, in the application to the lattice inverse problem [8,10], the modified Möbius inverse formula brings forward an analytic method to obtain reliable interatomic potentials from ab initio cohesive energy curves, and the obtained potentials with this method have been successfully applied to some calculation on intermetallics with a variety of structures [10–20], such as lattice dynamics [11–17], the field-ion microscopy image of Fe_3Al analysis [18], the site preference of ternary additions in Ni_3Al and Fe_3Al [19], the calculation of vibrational entropy for Fe–Al compounds [20], the site preference of foreign atoms in rare-earth intermetallics [21–23], and so on.

In this paper, Chen's lattice inversion method is extended to the calculation of interatomic potentials in the zinc-blende-type binary compounds with virtual structure technique. The calculation of the interatomic potentials in c-BN is taken as an example. c-BN is an artificial superhard material which has the highest hardness except for diamond and has similar thermal conductivity and better chemical inertia relative to diamond. It is a promising material for optoelectronic and microelectronic devices under high pressure and high temperature or in an aggressive environment [24]. A variety of theoretical investigations on c-BN have been presented during the past decade [25–31]. For example, Wentzcovitch et al. [25,26] studied its electronic and structural properties under different pressure, Rodriguez-Hernandez et al. [27] evaluated the elastic constants and energy band structure of BN using the total-energy pseudopotential technique with the local density approximation (LDA), Karch and Bechstedt [28] calculated the ab initio lattice dynamics of BN and BP using a plane wave pseudopotential method within the

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density-functional theory, Parlinski [29] calculated the lattice dynamics of BN by the density functional theory and the direct method, and Leite Alves et al. [30] calculated the lattice dynamics of BN using a 10-parameter shell model based on the first principle calculations.

2. Outline of the first principle pseudopotential calculation

In this work, the virtual structure technique is adopted in order to obtain the non-empirical interatomic pair potentials in c-BN. We calculate the dependence of cohesive energy (for three structures) on the lattice constants (see Fig. 1) and the dependence of the total energy on lattice distortion (see Fig. 2). The lattice constants, cohesive energy, bulk modulus and elastic constants are obtained based on the data of Figs. 1 and 2. The calculated data and the comparison with the previous work are listed in Table 1. The Mülliken charge of c-BN is $0.64e$, which is taken as the approximate effective charge of B and N in c-BN and causes the Coulomb interaction between B and N in our following calculations.

In our calculations, the first principle norm-conserving pseudopotential with the LDA is used. The crystal wave function is expanded using the plane-wave basis set, and the cut-off energy for plane-wave is 780 eV. The electronic minimization scheme is the density mixing with the conjugate gradient (CG) method for eigenvalue minimization. In the calculation of the total energy and charge density with density functional theory, a uniform mesh of k points in the irreducible Brillouin zone is produced by the Monkhorst–Pack scheme [32]. The quality of this representation can be verified by increasing the density of k points used in the mesh. The self-consistent iteration of the total energy is converged to 2×10^{-6} eV/atom in our calculations. To obtain the ab initio cohesive energy, the total energy at infinite lattice constant is set as the zero of cohesive energy. The total energy at infinite lattice constant is the extrapolated value by fitting the curve of the calculated total energy with lattice constants. Given the fact that an accurate calculation method is still an expectation and the experimental cohesive energy data for III–V
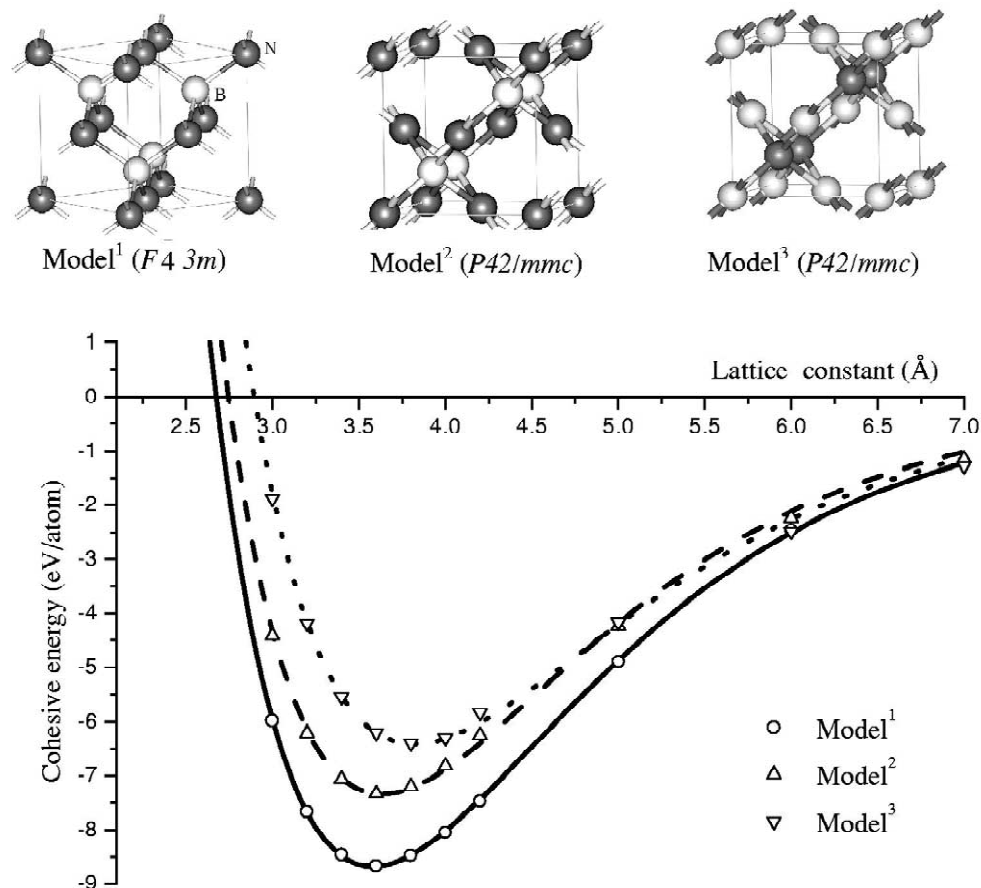
Fig. 1. The cohesive energy of BN (for three structures) obtained with the first principle pseudopotential technique. The ab initio values of lattice constant, cohesive energy and bulk modulus acquired from the cohesive energy curves of c-BN are listed in Table 1.
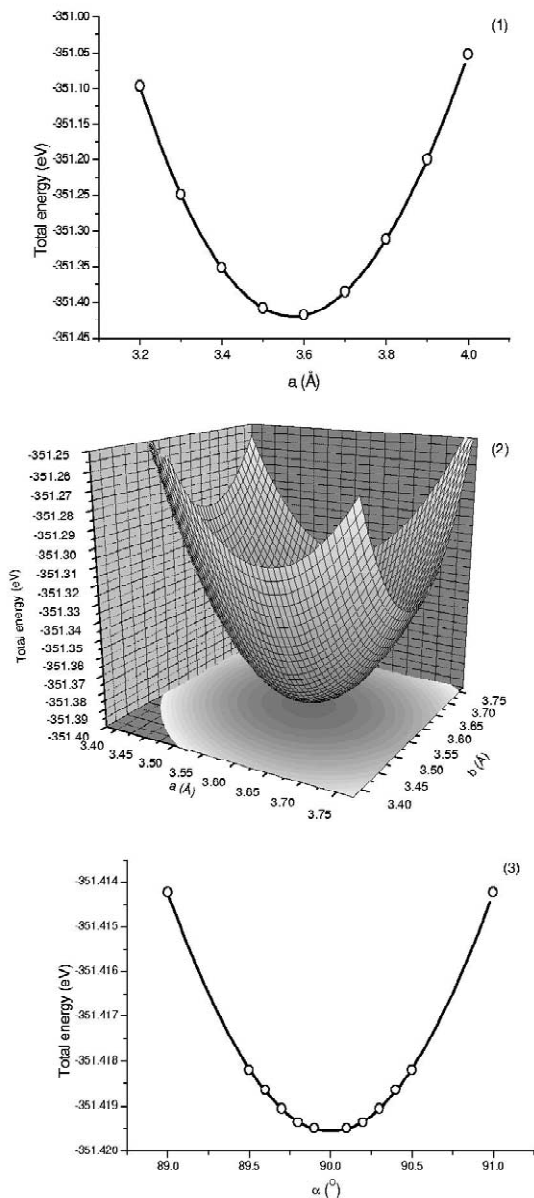
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125 Fig. 2. The dependence of the total energy on the lattice distortion
126 obtained by the first principle pseudopotential technique. The corre-
127 sponding ab initio values of c_{11}, c_{12}, c_{44} are listed in Table 1. (1)
128 $b = c = a_0$, $\alpha = \beta = \gamma = 90°$, E_{tol} vs. a; (2) $c = a_0$, $\alpha = \beta = \gamma = 90°$, E_{tol}
129 vs. (a,b); (3) $a = b = c = a_0$ $\beta = \gamma = 90°$, E_{tol} vs. α.

145 compounds are so scarce up to now [33], the cohesive
146 energy based on the LDA is adopted in our calculation.

3. The interatomic potentials of c-BN   147

3.1. Chen's lattice inversion method and the virtual   148
lattice technique   149

150 In general, any interatomic pair potential can be ob-
151 tained by strict lattice inversion from ab initio cohesive
152 energy [8]. Suppose that the cohesive energy of elemental
153 crystal can be expressed as the sum of interatomic pair
154 potentials:

$$U(x) = \frac{1}{2}\sum_{n=1}^{\infty} r_0(n)\,\Phi(b_0(n)x) \tag{1}$$ 155

156 where x is the nearest-neighbor distance, $r_0(n)$ is the
157 number of the nth set of lattice points, $b_0(n)x$ is the
158 distance of the nth set of lattice points. $\Phi(x)$ is the pair
159 potential function. The series $\{b_0(n)\}$ can be extended into
160 a multiplicatively closed semi-group $\{b(n)\}$. Then Eq. (1)
161 can be written as

$$U(x) = \frac{1}{2}\sum_{n=1}^{\infty} r(n)\,\Phi(b(n)x) \tag{2}$$ 162

163 where

$$r(n) = \begin{cases} r_0(b_0^{-1}[b(n)]) & b(n) \in \{b_0(n)\} \\ 0 & b(n) \notin \{b_0(n)\} \end{cases} \tag{3}$$ 164

165 Thus the pair potential from inversion can be written as

$$\Phi(x) = 2\sum_{n=1}^{\infty} I(n)U(b(n)x) \tag{4}$$ 166

167 where $I(n)$ is determined by

$$\sum_{b(d)\,\big|\,b(n)} I(d)r\left(b^{-1}\left[\frac{b(n)}{b(d)}\right]\right) = \delta_{n1}. \tag{5}$$ 168

169 There are three types of pair-potentials Φ_{B-B}, Φ_{N-N} and
170 Φ_{B-N} for c-BN. It is unreasonable to apply the potentials
171 Φ_{B-B} and Φ_{N-N} obtained from the elemental crystal
172 directly to the c-BN due to the difference of bond-types.

130 Table 1
131 Comparison of calculated properties for c-BN in this paper with those in previous work
132

		Previous works				Ab initio	The values by interatomic potentials	
		[40]	[30]	[27]	[25]	values	Pair only	Pair and 3-body
Lattice constant (Å)		3.6155	3.625	3.575	3.606	3.581	3.581	3.581
Cohesive energy (eV/atom)						8.677	8.605	8.605
Bulk modulus (10^{11} N/m^2)			3.71	4.1	3.67	4.038	4.037	4.037
Elastic constants	c_{11}	7.12		8.44		7.824	3.792	7.832
(10^{11} N/m^2)	c_{12}			1.9		1.852	4.159	2.139
	c_{44}			4.83		5.234	1.269	4.505

190 Firstly, we suppose the potentials are transferable between
191 the structures with space groups $F\bar{4}3m$ and $P42/mmc$. It is
192 seen from Fig. 1 that the N sub-lattice and the relative
193 displacement of N and B atoms in model[1] are identical to
194 that in model[2], respectively. So the cohesive energy
195 difference at the same lattice constant between model[1] and
196 model[2] is determined only by the interatomic interaction
197 Φ_{B-B}. Based on the cohesive energy difference with
198 different lattice constants, the interatomic potential Φ_{B-B} is
199 obtained using Chen's lattice inversion method. Similarly,
200 Φ_{N-N} can be obtained from the cohesive energy difference
201 between model[1] and model[3]. Subsequently, the potential
202 Φ_{B-N} can be calculated by the dependence of the cohesive
203 energy of c-BN on the lattice constants. Then all the
204 necessary interatomic pair potentials are obtained employ-
205 ing Chen's lattice inversion method. The results are shown
206 in Fig. 3. It is appropriate that the interatomic pair
207 potentials Φ_{B-B}, Φ_{N-N} and Φ_{B-N} can be described approxi-
208 mately by the following function

209 $$\Phi_{p(B-N)} = D_0\left(e^{-2\alpha(r-R_0)} - 2e^{-\alpha(r-R_0)}\right) + \frac{Q_B Q_N}{4\pi\varepsilon_0 r}\,\mathrm{erfc}\left(\frac{r}{\beta}\right)$$

210 $$\tag{6}$$

211 $$\Phi_{p(B-B\ or\ N-N)} = D_0 e^{-\alpha(r-R_0)} + \frac{Q_B^2}{4\pi\varepsilon_0 r}\,\mathrm{erfc}\left(\frac{r}{\beta}\right) \tag{7}$$

212 where r is the interatomic interaction distance, D_0, α, R_0,
213 β are the potential parameters, Q_B and Q_N, the Mülliken
214 charge obtained from the first principle calculation, are the
215 approximate effective charge of B atom and N atom,
216 respectively, and $\mathrm{erfc}(x)$ is the complementary error func-
217 tion. The pair potentials are shown in Fig. 3 and Table 2.

218 *3.2. Determination of three-body potentials for c-BN*

219 From Table 1, one can see that c-BN under the pair
220 potentials interaction does not satisfy the Born stability

Table 2
The parameters of the interatomic pair-potentials for c-BN. The effective
charge of the B and N atom is $\pm 0.64e$, respectively

	B–B	N–N	B–N
D_0 (eV)	2.028	2.030	4.575
α (1/Å)	1.707	2.457	1.959
R_0 (Å)	2.113	2.108	1.472
β (Å)	2.801	2.801	2.801
$R_{cut\text{-}off}$ (Å)	10.3	10.3	10.3

conditions of a cubic crystal, i.e. $c_{ij} > 0$ and $c_{11} - c_{12} > 0$,   221
which results in the zinc-blende structural 'collapse' for a   222
small vibration of the atoms. So the three-body term, a   223
supplement to the isotropic two-body potentials, is neces-   224
sary for the accurate description of the interatomic interac-   225
tions in zinc-blende structure. In this paper, the MSW   226
[34,35] three-body potential is adopted as a necessary   227
modification to the pair potentials   228

$$\Phi_3(r_{ij}, r_{ik}, \theta_{jik}) =$$ 229

$$\begin{cases} \lambda_i \exp\left[\dfrac{\gamma_i}{(r_{ij} - r_i^c)} + \dfrac{\gamma_i}{(r_{ik} - r_i^c)}\right]\left(\cos\theta_{jik} - \cos\theta_{jik}^c\right)^2 & r_{ij} < r_i^c \text{ and } r_{ik} < r_i^c \\ 0 & \text{otherwise} \end{cases}$$ 230

$$\tag{8}$$ 231

where λ_i, γ_i, r_i^c and θ_{jik}^c are constants and θ_{jik} is the angle   232
subtended by r_{ij} and r_{ik} with the vertex at i. The function   233
$\Phi_3(r_{ij}, r_{ik}, \theta_{jik})$ determines the three-body contribution to   234
atom i that comes from the effect between three atoms i, j 235
and k, with i as the central atom and j and k as two of its   236
covalently bonded neighbors. The value of r_i^c is between   237
the value of nearest distance and value of next-nearest   238
distance. MSW three-body potential is widely applied in   239
investigations such as the surface, interface, defect, me-   240
chanical property and melting etc. [34,35]. Here, $\theta_{jik} =$ 241
$\arccos(-1/3)$. Obviously, MSW three-body potential has   242
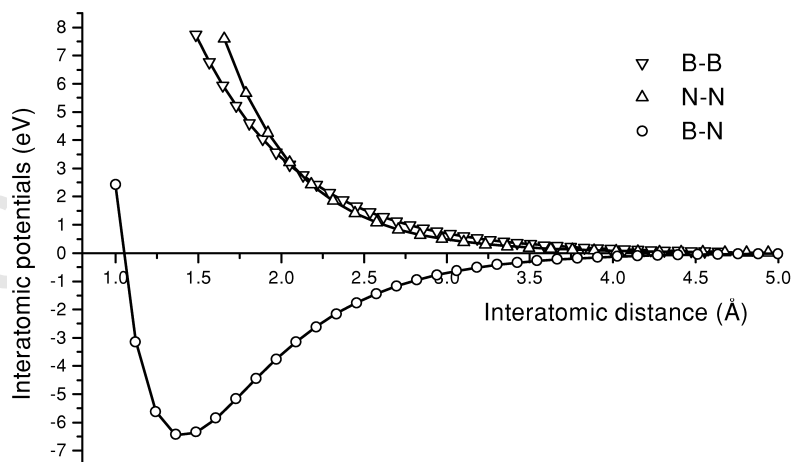
175

176 Fig. 3. The interatomic pair potentials of B–B, N–N and B–N acquired from ab initio cohesive energy curves in Fig. 1 with Chen's lattice inversion
177 method. ($\bigcirc$, $\triangle$, $\triangledown$ correspond to the data by Chen's lattice inversion method, and the line is the fitted result of formula (6) or (7)).

Table 3
The parameters of MSW 3-body potentials for c-BN

	N–B–N	B–N–B
λ_i (eV)	943.710	1287.96
γ_i (Å)	1.5415	1.5415
r_i^c (Å)	2.0867	2.0867

no contribution to the cohesive energy either for the zinc blende structure with space group $F\bar{4}3m$ or for the virtual structures with space group $P42/mmc$. It operates only when the atom deviates from the lattice points or has the trend to deviate. So the adoption of MSW three-body potential can be logically self-consistent with our previous pair potential calculational method.

Based on the pair potential parameters, the contribution of the pair potentials to the elastic constants is calculated. Furthermore, the components of the elastic constants contributed by three-body potentials $c_{ij,3\text{-body}} = c_{ij} - c_{ij,\text{pair}}$ are evaluated using the ab initio values of c_{ij}. Then the MSW three-body potential parameters are determined by fitting the $c_{ij,3\text{-body}}$. The results are listed in Table 3.

4. The application of interatomic potentials in c-BN

4.1. Basic check

The lattice constants, bulk modulus and the elastic constants of c-BN are evaluated according to the calculated interatomic potentials. The results are listed in Table 1.

4.2. The lattice dynamics for c-BN

Many researchers have studied the phonon spectra of the materials with III–V compounds. They measured the phonon spectra by nonelastic neutron scattering, then through constructing an empirical model and adjusted the interatomic force constants to match their calculation to experiments. Others determined the force constants by a first principle calculation. In general, a better fitting needs 11–14 near-neighbor interatomic force constants. These methods result in uncertainty for the forms and values of the interatomic force constants to some extent. In this paper, based on the interatomic potentials without disposable parameters obtained from Section 3, the phonon dispersion of c-BN is calculated using the Born–von Karman model (see Fig. 4).

In our calculation, the Mülliken charge is taken as the effective charge of the B atom and N atom and the screening Coulomb potential is employed to describe the electrostatic interaction approximately. This approximation results in the degeneration of phonon LO and TO frequencies at $q=0$, as given in Fig. 4 while the experimental results show that the LO and TO are split. The deviation of the calculation from experiments will be eliminated when
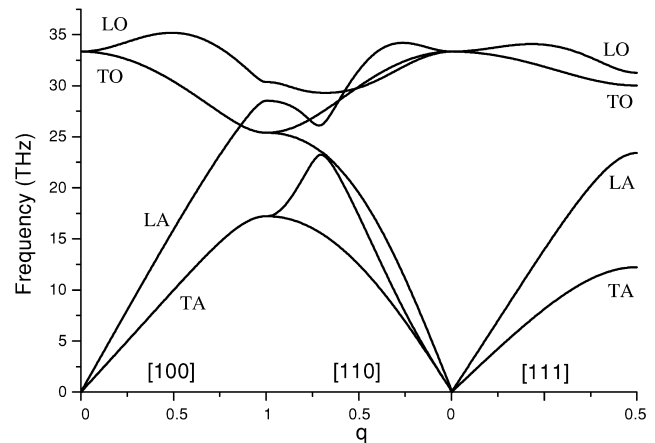
Fig. 4. The c-BN phonon dispersion calculated by the interatomic potentials and Born–von Karman model (the experimental data in Ref. [30] gives $\Omega_{\text{LO}}^{\text{BN}} = 39.12$ THz, $\Omega_{\text{TO}}^{\text{BN}} = 31.62$ THz).

the effective charges of the B atom and N atom are increased and the electrostatic interaction is summed with the Ewald method [36]. However, the use of the adjustable effective charge will not preserve the characteristics of obtaining the interatomic potentials from the ab initio calculations without any disposable parameters in this work.

In general, the interatomic effect is very complex, quantum theory is indispensable for a strict analysis of this effect. Effective interatomic potentials are limited for an accurate description of this effect, particularly for the long-distance interatomic effect [37]. The lattice vibration is a dynamic quantity, and during vibration, the dipole and quadrupole moments will occur and interact with each other. But this interaction is not covered in our interatomic potentials.

5. Discussion

It has been an intractable problem to obtain the interatomic potentials of binary alloys and compounds. Generally, the interatomic potentials of the element crystal are directly transferred to the alloys, which are verified as a feasible approximate method by calculations [10,18–22]. However, for covalent and ionic crystals, the same transfer is not appropriate due to the large difference between the bond-types. The investigation of the interatomic potentials for ionic crystals is only limited in the empirical scheme. For example, a common model is the Buckingham potential or the Lennard–Jones potential attached to the Coulomb potential [38,39].

This paper has presented an exact inversion method to analytically obtain the interatomic pair-potentials for materials with the zinc-blende structure based on first principle calculations. The uncertainty in the empirical method to determine potential parameters is eliminated. Particu-

larly, the introduction of the virtual lattice structures is creative in obtaining the interatomic potentials from the calculated cohesive energy by a first principle calculation with Chen's inversion method.

In this paper, based on the two-body and three-body interatomic potentials mentioned above, the phonon dispersion of c-BN is evaluated with the Born–von Karman model. In our calculations, the screening Coulomb potential is employed to describe the electrostatic interaction approximately. The many-body interaction is simplified as MSW three-body potentials. These approximations may result in a little difference between our calculations and experiments. For lattice dynamics of BN, there are some excellent studies based on first-principles calculations by Parlinski [29], Karch, Bechstedt [28] and Leite Alves [30]. However, in this paper, Chen's lattice inversion method is extended to obtain the interatomic potentials of III–V compounds. It does open a door to expediently explore the structural, mechanical and thermodynamical properties of these materials based on ab initio calculations without disposable parameters.

Acknowledgements

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